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Tritylsulfinylamine: A New Member in the Family of Sulfinylamines

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Dedicated to Prof. Neil Bartlett on the occasion of his 70th birthday.

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Abstract

Triphenylmethyl N-sulfinylamine (trityl-NSO) was prepared from the reaction of trityl amine and SOCl₂. Trityl-NSO was characterized by ¹H, ¹³C, and ¹⁴N NMR spectroscopy in

CH₂Cl₂ solution and by Raman and infrared spectroscopy in the solid state. Crystals of trityl-NSO were grown from n-heptane and characterized by single crystal X-ray diffraction (*P*1, *a* = 8.9642(9) Å, *b* = 9.2135(9) Å, *c* = 11.0645(11) Å, α = 93.578(2)°, β = 101.098(2)°, γ = 118.142°, *Z* = 2, and *R*_{int} = 0.0332 at 223 K). Trityl-NSO represents the first alkyl *N*-sulfinylamine that has been fully structurally characterized.

Keywords: Triphenylmethylsulfinylamine; Vibrational spectroscopy; NMR spectroscopy, Crystal structure

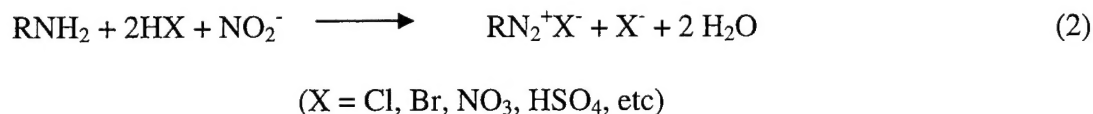
1. Introduction

There has been much recent interest in polynitrogen chemistry [1-9]. The successful synthesis of the N₅⁺ cation [10, 11] and the recent experimental detection of the N₅⁻ [12] anion by cleavage of *p*-hydroxyphenylpentazole prompted us to search for methods to prepare N₅⁻ salts in bulk. Since alkylpentazoles might be cleaved more readily than arylpentazoles, and diazonium salts are the precursors required for the preparation of pentazoles [13] (eq 1),

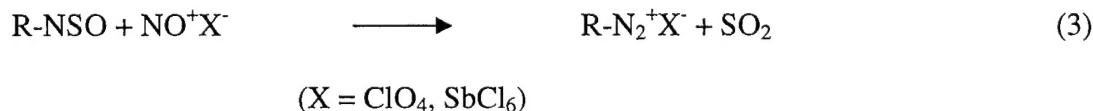


we became interested in the preparation of new alkyldiazonium salts. One of our targets in this area was the triphenylmethyldiazonium cation because of the exceptional stability of the triphenylmethyl (trityl) cation which would be formed as a by-product in the cleavage reaction of the C-N bond of the corresponding pentazole. Since the triphenylmethyldiazonium cation is unknown, methods for its synthesis were explored.

The synthesis of diazonium salts usually involves the reaction of nitrite with aryl amines in aqueous acids (eq 2).



However, this method cannot be used for trityl amine because the highly electrophilic carbon center of the methyl group is readily attacked by HX. Therefore, alternate methods were sought for the preparation of trityl-N₂⁺. One way to prepare diazonium salt under anhydrous, acid-free conditions employs the reaction of R-NSO with NO⁺ [14] (eq. 3).



While more than 600 *N*-sulfinylamine compounds are known, trityl-NSO has not been reported. In the present paper, we report the preparation and full characterization of trityl-NSO.

2. Experimental Section

2.1. Materials and Apparatus

Reactions were carried out in Pyrex glass vessels closed by grease-free Kontes glass-Teflon valves. Volatile materials were handled on a Pyrex glass vacuum line equipped with the

same valves. Nonvolatile solids were handled in the dry argon atmosphere of a glove box. Infrared spectra were recorded on a Midac, M Series, FT-IR spectrometer using KBr pellets. The pellets were prepared inside the dry box using an Econo press (Barnes Engineering Co.). Raman spectra were recorded on a Bruker Equinox 55 FT-RA spectrometer using a Nd-Yag laser at 1064 nm and Pyrex melting point capillaries as sample containers. Nuclear magnetic resonance spectra were recorded unlocked on a Bruker AMX 500 NMR spectrometer at room temperature. The ^1H , ^{13}C (^{14}N) NMR spectra were referenced to external samples of neat TMS (neat nitromethane).

The starting materials, $(\text{C}_6\text{H}_5)_3\text{CCl}$ (Aldrich), NH_3 (Aldrich, anhydrous, 99,99%), SOCl_2 (Aldrich), Et_3N (Aldrich), were used without further purification. Tritylamine, $(\text{C}_6\text{H}_5)_3\text{CNH}_2$, was prepared by literature methods [15]. The CH_2Cl_2 (Mallinckrodt) and n-heptane (Aldrich, anhydrous 99%) were dried over molecular sieves.

2.2. Preparation of $(\text{C}_6\text{H}_5)_3\text{CNSO}$

In a typical experiment, a 15 mm diameter H-shaped Pyrex glass vessel with a frit, equipped with two concentric grease-free Teflon valves (Kontes) was loaded inside the glove box with $(\text{C}_6\text{H}_5)_3\text{CNH}_2$ (1.989 mmol). Approximately 3 mL of CH_2Cl_2 was condensed onto the solid at -196°C , which dissolved completely upon warming to room temperature. At -196°C , 0.403g (3.98 mmol) NEt_3 was distilled onto the frozen CH_2Cl_2 solution and allowed to warm to room temperature yielding a clear colorless solution. A stoichiometric amount of SOCl_2 (1.98 mmol) was added in three increments followed by stirring for ca. 1 h. After the first addition, white $\text{HNEt}_3^+\text{Cl}^-$ started to precipitate. The solution was stirred for further 18 h at room temperature resulting in a deep brown suspension. Removal of all volatile material under vacuum

was followed by repeated (20 times) extractions of the solid with a few mL n-heptane. Each time the n-heptane solution had been filtered through the frit, the n-heptane solvent was condensed back onto the solid at -196 °C in a static vacuum. The filtrate residue consisted of pale brown, solid $(C_6H_5)_3CNSO$ (0.5288g , 1.732mmol, 87% yield).

2.3. Crystal Growth of $(C_6H_5)_3CNSO$

Inside the dry box, 0.011g of $(C_6H_5)_3CNSO$ (0.036 mmol) was loaded into a Pyrex glass vessel closed by a grease-free Teflon valve. n-Heptane (0.75 mL) was distilled onto the solid and most of it dissolved upon warming to room temperature. The solution was placed in an ethanol bath at -20 °C resulting in crystal growth. The n-heptane was slowly removed between -20 and -10 °C in a dynamic vacuum, resulting in further crystal growth.

2.4. Crystal Structure Determination of $(C_6H_5)_3CNSO$

The single crystal x-ray diffraction data of Ph_3CNSO were collected on a Bruker 3-circle platform diffractometer equipped with a SMART CCD (charge coupled device) detector with the χ -axis fixed at 54.74° and using MoK_{α} radiation ($\lambda = 0.71073 \text{ \AA}$) from a fine-focus tube. This diffractometer was equipped with an LT-3 apparatus for low temperature data collection using controlled liquid nitrogen boil off. A few reasonably well-formed single crystals were selected in a glove-box, equipped with a CCD camera mounted microscope. The crystals were coated with epoxy grease and then mounted on a magnetic goniometer head. Cell constants were determined from 90 ten-second frames. A complete hemisphere of data was scanned on omega (0.3°) with a run time of thirty-second per frame at a detector resolution of 512 x 512 pixels using the SMART software [16]. A total of 1271 frames were collected in three sets and a final set of 50

frames, identical to the first 50 frames, were also collected to determine any crystal decay. The frames were then processed on a PC, running on Windows NT software, by using the SAINT software [17] to give the hkl file corrected for Lp/decay. The absorption correction was performed using the SADABS [18] program. The structure was solved by the direct method using the SHELX-90 program and refined by the least squares method on F^2 , SHELXL-97 incorporated in SHELXTL Suite 5.10 for Windows NT [19]. All atoms were refined anisotropically. For the anisotropic displacement parameters, the $U(eq)$ is defined as one third of the trace of the orthogonalized U_{ij} tensor. The hydrogen atoms were located from difference electron density maps and refined in an isotropic manner.

3. Results and Discussion

3.1. Synthesis and spectroscopic characterization of $(C_6H_5)_3CNSO$

Trityl-NSO was prepared following the method of Michaelis [20] which is based on the reaction of RNH_2 with $SOCl_2$. The product was isolated in 87% yield by repeated extractions with n-heptane, yielding a pale brown solid with a melting point of 89 to 89.5 °C. Its purity was ascertained by IR, Raman and NMR spectroscopy. The IR and Raman spectra of trityl-NSO are shown in Fig. 1, and the vibrational frequencies are listed in Table 1 together with assignments for selected vibrations. Since the trityl skeleton gives rise to a complex vibrational spectrum, Raman spectra of a series of trityl compounds were recorded (Table 1), leading to the unambiguous identification of the vibrational frequencies associated with the NSO group. A thorough study of N-sulfinyl-benzamine [21] showed that the N=S and the S=O stretching vibrations are strongly coupled and that the NSO group gives rise to an out-of-phase and an in-

phase stretching mode. In trityl-NSO, the $\nu_{\text{as}}(\text{NSO})$ and the $\nu_{\text{s}}(\text{NSO})$ vibrations are assigned to 1294 cm^{-1} and 1123 cm^{-1} , respectively. In addition, the deformation mode, $\delta(\text{NSO})$, could be assigned to the band at 585 cm^{-1} .

The ^1H , ^{13}C and ^{14}N NMR spectroscopic data are listed in Table 2. The ^1H and ^{13}C NMR chemical shifts lie in the region expected for the triphenylmethyl group. The broad ^{14}N resonance for N-sulfinylamines at -39 ppm ($\Delta\nu_{1/2} = 700\text{ Hz}$) is in the range observed for organic sulfinylamines [22].

3.2. Crystal Structure of $(\text{C}_6\text{H}_5)_3\text{CNSO}$

Details of the crystal data for $(\text{C}_6\text{H}_5)_3\text{CNSO}$ are provided in Table 3; the atomic coordinates and equivalent isotropic displacement parameters are listed in Table 4; and the observed bond lengths, angles, and contacts are listed in Table 5.

The tritylsulfinylamine crystallizes in the triclinic space group $P\bar{1}$ and is the first structurally characterized aliphatic derivative containing an NSO group. Three phenyl groups bonded to the tertiary carbon are oriented in a propeller-like fashion as shown in Fig. 2. The NSO group is oriented closest to the C(2)-C(7) phenyl ring as seen from the S(1)-N(1)-C(1)-C(2) torsion angle of $40.3(2)^\circ$. For the other two phenyl rings, this torsion angle increases to $82.1(2)^\circ$ and $159.5(1)^\circ$ for S(1)-N(1)-C(1)-C(8) and S(1)-N(1)-C(1)-C(14), respectively. The N=S=O angle of $122.61(8)^\circ$ is also the largest known angle out of all the reported structures containing an uncoordinated terminal NSO group [23-30]. The next closest NSO angle reported is 121.87° for 2,4,6-tri-*t*-butyl-N-sulfinylaniline [25]. The CNSO fragment possesses the expected *syn* configuration [31] with respect to the SN double bond. The crystal lattice does not show any short-range intermolecular contacts, the closest one being $\text{H}(12)\cdots\text{O}(1)(-1+x,-1+y,z)$ $2.75(3)\text{ \AA}$.

However, there are intramolecular hydrogen bonds [32] resulting from S(1), O(1) and N(1) i.e., $S(1)\cdots H(15) = 2.93(2)$, $S(1)\cdots H(3) = 3.00(2)$ Å, $O(1)\cdots H(15) = 2.57(2)$ Å and $N(1)\cdots H(13) = 2.35(2)$ Å. The NSO groups show dimer formation via the $S(1)\cdots O(1)$ ($-x, 1-y, 1-z$) contacts at $3.299(2)$ Å (Fig. 2) which is roughly equal to the sum of the van der Waal radii for sulfur (1.8) and oxygen (1.52 Å).

Conclusion

While more than 600 *N*-sulfinylamines are known, triphenylmethyl *N*-sulfinylamine represents only the 13th example of an organic sulfinylamine and the first example of an alkyl *N*-sulfinylamine that has been fully structurally characterized by single crystal X-ray diffraction. The $N=S=O$ angle of $122.61(8)^\circ$ is the largest known angle out of all the reported structures containing an uncoordinated terminal NSO group. In spite of the complexity of the vibrational spectra of trityl-NSO, the vibrational frequencies associated with the NSO group could be assigned.

Acknowledgements

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Supplementary material

Tables of structure determination summary, atomic coordinates, bond lengths and angles and anisotropic displacement parameters of $(\text{C}_6\text{H}_5)_3\text{CNSO}$ in CIF format has been sent to Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1 EZ, UK as supplementary material No. SUP NB1-22 (28 pages) and can be obtained by contacting the CCDC (quoting the article details and the corresponding SUP number).

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Table 1
Vibrational Spectra of $(C_6H_5)_3CNSO$ Compared to the Raman Spectra of Related Trityl Compounds.^a

$(C_6H_5)_3CNH_2$	$(C_6H_5)_3CCl$	$(C_6H_5)_3CN_3$	$(C_6H_5)_3COH$	$(C_6H_5)_3CNF_2$	$(C_6H_5)_3CNSO$ Raman	IR
3367(2)						$\nu(NH_2)$
3301(4)						
3192(2)	3193(1)	3194(1)	3198(<0.5)	3195(2)	3189(1)	
3158(2)	3161(3)	3162(1)	3166(1)	3161(3)	3164(2)	3101(w)
3072sh(40)						3084(m)
3064(63)	3068(78)	3065(86)	3068(65)	3076(76)	3067(64)	3063(m)
3045(42)	3056(52)sh			3065(56)sh	3058(42)sh	3056(sh)
	3038(10)	3038(1)		3043(11)	3036(8)	3032(m)
3023(9)	3023(8)	3024(1)		3026(7)	3023(7)	3021(m)
3001(3)	3004(4)	3004(1)	3007(2)	3003(6)	3004(4)	3002(m)
2971(3)	2971(4)	2973(2)	2986(2)	2978(4)	2977(3)	
	2924(1)		2937(10)	2914(2)	2936(1)	
	2897(1)	2906(1)			2905(1)	
				2894(1)	2890(1)	
2786(<0.5)	2769(1)	2772(<0.5)	2792(<0.5)		2774(<0.5)	
	2722(<0.5)					
2580(<0.5)	2576(1)	2569(1)	2585(1)	2568(1)	2570(<0.5)	
		2098(2)	2249(4)			
	1639(1)sh					$\nu_{as}(NNN)$
					1609sh	1604(sh)
1598(16)	1595(16)	1599(18)	1602(18)	1601(15)	1598(11)	1595(ms)
1583(7)	1584(10)sh	1585(3)	1586(3)	1589(8)sh	1585(8)	1582(sh)
		1490(1)	1499(<0.5)	1495(1)		1490(vs)
1445(1)	1448(1)	1450(2)	1450(2)	1447(1)	1449(1)	1448(vs)
						1445(vs)
		1380(1)	1377(<0.5)			1393(m)
	1321(1)	1326(1)	1345(1)	1338(1)	1328(1)	1325(ms)
1302(<0.5)	1303(<0.5)		1300(<0.5)			
	1284(1)	1282(1)		1283(<0.5)	1294(5)	1292(vs) $\nu_{as}(NSO)$
		1263(3)				1283(vs)
						$\nu_s(NNN)$
1217(3)	1213(4)			1219(2)		
	1203(4)					1194(s)
1186(13)	1187(11)	1188(8)	1199(7)	1193(10)	1189(10)	1188(s)
						1180(s)
1163(10)	1159(10)	1167(3)	1173(12)		1164(5)	1161(m)
1159(11)	1149(23)	1157(12)		1152(13)	1152(7)	1150(m)
					1123(23)	1124(vs) $\nu_s(NSO)$
1094(1)	1084(1)	1087(1)	1087(2)	1082(1)	1085(2)	1083(s)
1078(1)						
1057(2)					1065(1)	
1029(17)	1034(20)	1033(19)	1039(18)	1036(17)	1034(17)	1037(ms)
						1033(ms)
1004(65)	1003(54)	1002(68)	1005(66)	1004(35)	1003(40)	1002(ms)
	988sh			991(15)	995sh	991(w)
						985(w)
				965(3)	975(1)	976(w)

Table 1(contd.)

Vibrational Spectra of $(\text{C}_6\text{H}_5)_3\text{CNSO}$ Compared to the Raman Spectra of Related Trityl Compounds.^a

$(\text{C}_6\text{H}_5)_3\text{CNH}_2$	$(\text{C}_6\text{H}_5)_3\text{CCl}$	$(\text{C}_6\text{H}_5)_3\text{CN}_3$	$(\text{C}_6\text{H}_5)_3\text{COH}$	$(\text{C}_6\text{H}_5)_3\text{CNF}_2$	$(\text{C}_6\text{H}_5)_3\text{CNSO}$ Raman	IR
954(1)				952(3)	945(2)	942(w)
920(1)	932(1)	949(2)	927(3)	927(2)	936(3)	933(w)
910(1)	896(3)	900(3)		914(2)	906(2)	904(s)
					898(4)	898(vs)
			877(3)	881(1)		
867(2)				858(4)	861(<0.5)	
849(1)	849(2)	844(1)		848(3)sh		850(m)
	820(5)					847(m)
						763(vs)
767(2)	766(1)	762(1)	766(2)	771(1)	755(2)	758(vs)
754(1)	741(1)	741(1)		748(<0.5)		747(vs)
				711(4)		703(vs)
700(14)	703(1)	704(3)	701(12)	703(5)	689(10)	687(s)
	669(12)	670(4)		660(3)	653(2)	652(s)
					640(2)	639(vs)
629(3)	629(3)					
620(9)	619(6)	619(7)	621(9)	620(7)	621(7)	618(m)
585(1)				596(3)		
					585(2)	582(m) $\delta(\text{NSO})$
				541(5)		
533(2)		531(1)			533(2)	531(m)
	511(1)sh	508(1)		517(1)	509(1)	502(s)
	497(7)					
445(2)		455(2)	450(1)			
416(<0.5)	406(1)	411(4)			416(2)	416(s)
						413(s)
						412(s)
376(1)		386(<0.5)	384(2)		389(3)	
342(1)	350(23)	334(2)	354(<0.5)	362(4)		
311(3)	319(6)	316(1)	319(<0.5)	312(8)	324(2)	
		307(1)			304(2)	
281(8)	281(13)	280(9)	285(9)	286(12)	281(9)	
250(9)	245(5)		249(7)	263(10)	253(3)	
234(2)		238(9)		239(3)	243(2)	
208(4)	183(13)	214(5)		188(2)	209(9)	
				140(15)sh	160(8)	
				129(27)sh		
111(90)				117(35)sh	116sh	
99(100)	102(100)	103(100)	94(100)	95(100)	105(100)	

w = weak; m = medium; ms = medium strong; s = strong; vs = very strong; sh = shoulder. ^a All data from this study.

Table 2

¹H, ¹³C and ¹⁴N NMR Spectroscopic Data for (C₆H₅)₃CNSO in CH₂Cl₂.

		δ (ppm)	Δν _{1/2} (Hz)
¹ H		6.75 (m)	
¹³ C	o/m (C ₆ H ₅) ₃	128.19/128.62	
	p (C ₆ H ₅) ₃	127.64	
	ipso (C ₆ H ₅) ₃	144.50	
	C(C ₆ H ₅) ₃	80.98	
¹⁴ N		-39	700

Table 3

Crystal Data for (C₆H₅)₃CNSO.

chemical formula	C ₁₉ H ₁₅ N S O
fw	305.38
T, K	223(2)K
space group	triclinic <i>P</i> $\bar{1}$ (No. 2)
<i>a</i> , Å	8.9642(9)
<i>b</i> , Å	9.2135(9)
<i>c</i> , Å	11.0645(11)
α , deg	93.578(2)
β , deg	101.098(2)
γ , deg	118.142(2)
<i>V</i> , Å ³	778.24(13)
<i>Z</i>	2
ρ_{calc} , g cm ⁻³	1.303
μ , mm ⁻¹	0.209
R_1 , ^a wR_2 ^b [<i>I</i> > 2 σ (<i>I</i>)]	$R_1 = 0.0345$, $wR_2 = 0.0910$
R_1 , ^a wR_2 ^b (all data)	$R_1 = 0.0409$, $wR_2 = 0.0962$

$$^a R1 = (\Sigma(F_o - F_c)/F_o). \quad ^b wR2 = [\Sigma(w(F_o - F_c)^2)/\Sigma w/F_o^2]^{1/2}.$$

Table 4

Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($\text{\AA}^2 \times 10^3$) for $(\text{C}_6\text{H}_5)_3\text{CNSO}$.

	x	y	z	U(eq) ^a
O(1)	2025(2)	5053(2)	5284(1)	51(1)
S(1)	601(1)	3352(1)	4857(1)	35(1)
N(1)	83(2)	2101(2)	5706(1)	29(1)
C(1)	678(2)	2061(2)	7047(1)	24(1)
C(2)	1161(2)	3684(2)	7898(1)	26(1)
C(3)	132(2)	4433(2)	7655(2)	33(1)
C(4)	501(3)	5854(2)	8438(2)	43(1)
C(5)	1899(3)	6541(2)	9483(2)	45(1)
C(6)	2910(3)	5794(2)	9747(2)	44(1)
C(7)	2548(2)	4370(2)	8960(2)	34(1)
C(8)	-884(2)	573(2)	7349(1)	25(1)
C(9)	-1029(2)	490(2)	8571(2)	32(1)
C(10)	-2418(2)	-865(2)	8844(2)	41(1)
C(11)	-3677(3)	-2151(2)	7898(2)	46(1)
C(12)	-3543(2)	-2081(2)	6683(2)	46(1)
C(13)	-2158(2)	-734(2)	6406(2)	35(1)
C(14)	2246(2)	1761(2)	7130(1)	25(1)
C(15)	3739(2)	2953(2)	6824(2)	31(1)
C(16)	5132(2)	2689(2)	6826(2)	39(1)
C(17)	5072(2)	1239(2)	7143(2)	43(1)
C(18)	3622(2)	68(3)	7469(2)	45(1)
C(19)	2210(2)	322(2)	7463(2)	34(1)

^a U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor

Table 5

Experimental Bond Lengths [\AA] and Angles [$^\circ$] for $(\text{C}_6\text{H}_5)_3\text{CNSO}$.

O(1)-S(1)	1.450(1)	O(1)-S(1)-N(1)	122.61(8)
S(1)-N(1)	1.492(1)	C(1)-N(1)-S(1)	136.8(1)
N(1)-C(1)	1.486(2)	N(1)-C(1)-C(2)	111.8(1)
C(1)-C(2)	1.538(2)	N(1)-C(1)-C(8)	105.5(1)
C(1)-C(8)	1.542(2)	N(1)-C(1)-C(14)	105.3(1)
C(1)-C(14)	1.544(2)	C(2)-C(1)-C(8)	109.7(1)
C(4)-C(5)	1.382(3)	C(2)-C(1)-C(14)	112.5(1)
C(11)-C(12)	1.375(2)	C(8)-C(1)-C(14)	111.8(1)
C(16)-C(17)	1.382(2)	C(5)-C(4)-C(3)	120.2(2)

Figure Captions

Fig. 1. Infrared and Raman Spectra of $(\text{C}_6\text{H}_5)_3\text{CNSO}$.

Fig. 2. Structure of the $(\text{C}_6\text{H}_5)_3\text{CNSO}$ Molecule showing the Dimer Formation via $\text{S}\cdots\text{O}$ Contacts. Thermal Ellipsoids are shown at the 50% Probability Level.

Figure 1

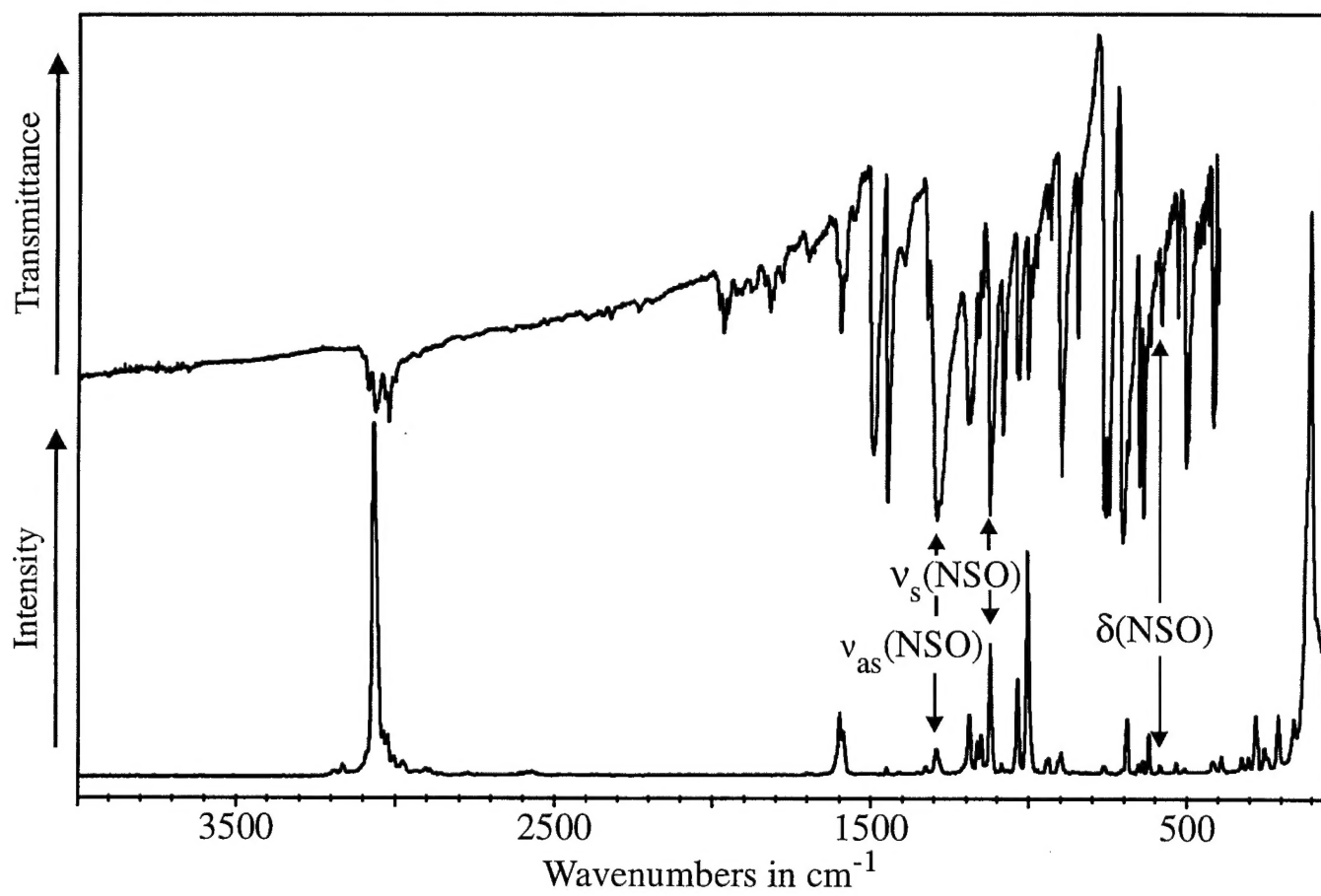
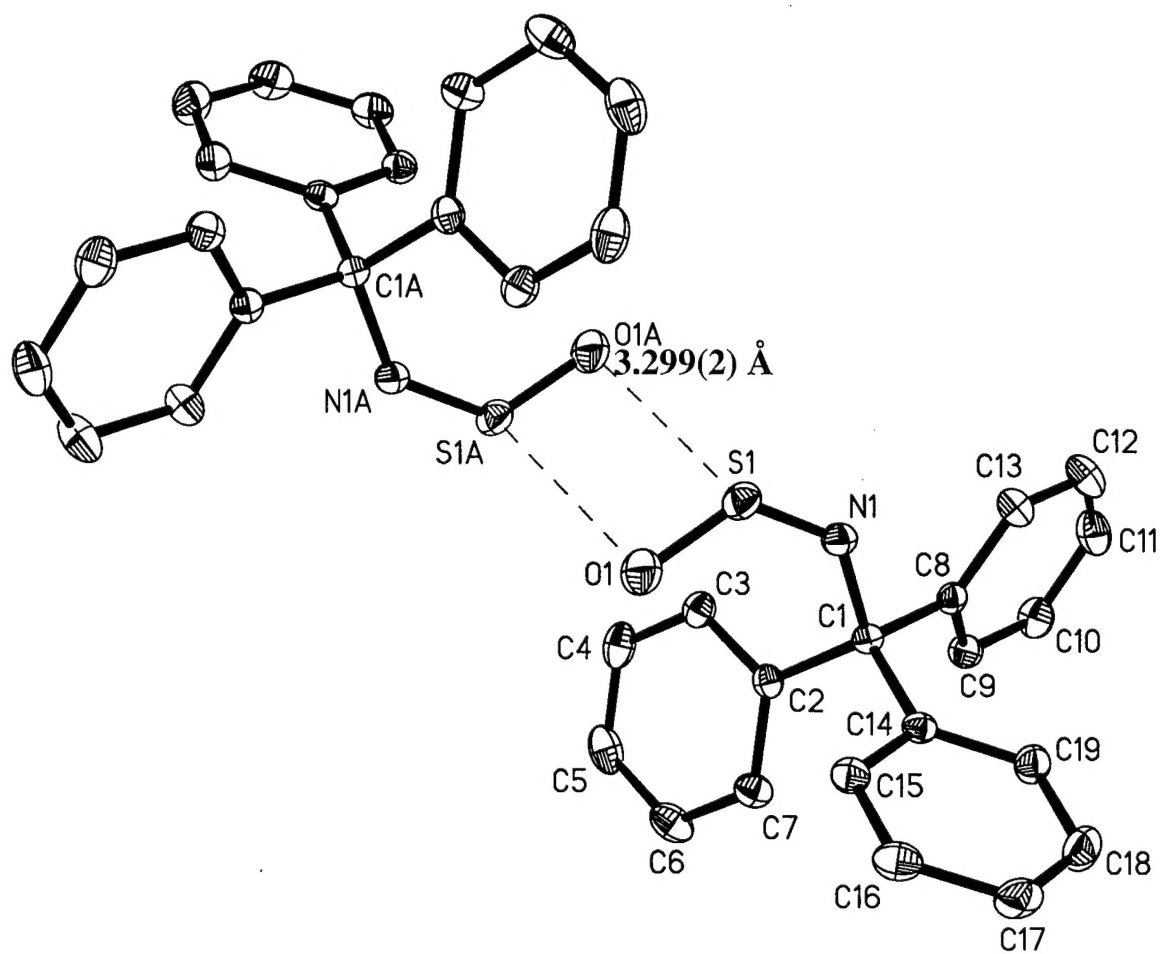


Figure 2



Tritylsulfinylamine: A New Member in the Family of Sulfinylamines

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